

THE INFLUENCE OF MECHANOCHEMICAL MODIFICATION ON PREVENTION OF TOXIC ABILITY OF HUMIC ACIDS TOWARDS PHENANTHRENE IN AQUATIC ENVIRONMENT¹M.P. Mirzobekzoda, ²E.V. Maltseva, ¹N.S. Shekhovtsova

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E-mail: maltseva2@gmail.com**ВЛИЯНИЕ МЕХАНОХИМИЧЕСКОЙ МОДИФИКАЦИИ НА ДЕТОКСИЦИРУЮЩУЮ СПОСОБНОСТЬ ГУМИНОВЫХ КИСЛОТ ПО ОТНОШЕНИЮ К ФЕНАНТРЕНУ В ВОДНЫХ СРЕДАХ**¹М.П. Мирзобекзода, ²Е.В. Мальцева, ¹Н.С. Шеховцова

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Annotation. Целью работы является количественная оценка взаимодействия фенантрена с модифицированными гуминовыми кислотами в водной среде. Изменение структуры и свойств ГК после модификации было изучено методами ИК-, ¹H ЯМР – спектроскопии и потенциометрического титрования. Доказано что применение тиомочевины в качестве модифицирующего агента значительно увеличивает связывающую способность гуминовых кислот по отношению к фенантрону.

Polycyclic aromatic hydrocarbons (PAH) – are organic compounds, consisting of three or more condensed aromatic rings and have particular interests regarding their toxic and cancerogenic properties [1]. Typical representative of PAH is phenanthrene, anthropogenic sources of which are coal tar, oil and products of its processing, cigarettes smoke, etc. Extended exposure to phenanthrene leads to the decrease of the amounts of hemoglobin in the blood and causes leucocytosis [2].

Up to date to purify water from phenanthrene and its compounds different oxidation methods are used (water oxidation with ozone, hydrogen peroxide and UV exposure), which are environmentally not friendly and costly [3]. Therefore, the effort is going towards finding new methods, which are based on organic compounds, like humic acids (HA).

Humic acids are natural compounds having a detoxifying ability towards organic pollutants. By work [4] for the first time was proven the relationship between aromaticity of humic acids and their detoxifying ability towards PAH. Prior research showed that mechanoactivation modifies the content and properties of humic acids, increasing their detoxifying abilities [5, 4].

Therefore, the main purpose of our work is the quantification of interaction of phenanthrene with modified humic acids in aquatic environments.

The research was focused on humic acids, which were extracted from transitional peat of Tomsk region (HA1). The peat was mechanically activated without any reagents (HA2) and mechanochemically modified in the presence of thiourea (HA3). The methods of IR-, ^1H NMR – spectroscopy and potentiometric titration were used to study the effects of mechanochemical modifications on the composition and acid – base properties of humic acids [7].

In the Tab. 1 presents the data about changes of fragments compositions of humic acids after mechanochemical modifications. According to our results, the above-mentioned humic acids consist of high

amounts of aromatic and carbohydrate portions. After the process of modifications the slight decline of the H_α

and H_β is taking place, which could be associated with breaks within carbons bonds. At the same time, the

increase of aromatic fragments in humic acids structure was observed (H_{Ar}).

Table 1

The fragment structure of modified humic acids according to ^1H NMR spectroscopy

Sample	Contain of hydrogen in structural fragments of HAs, %				
	H_{Ar}	$\text{H}_\alpha\text{-C-Ar,}$ $\text{H}_\alpha\text{-C=C-}$	$\text{H}_\beta\text{-C-C=C-}$	$\text{H}_\gamma\text{-C-R}$	$\text{H}_{\text{carbohyd.}}$
HA1	25,2	18,7	15,1	6,1	34,9
HA2	23,93	16,05	14,75	6,88	38,38
HA3	33,55	15,15	12,98	8,36	29,96

The increase portion of aromatic fragments in the structure of humic acids can lead to the affinity to PAH and increase the ability to detoxification.

For the quantity analysis of interaction of phenanthrene with modified humic acids in aquatic environment were used the method of molecular spectrophotometry. The experiment was conducted comparing the absorbance of the standard and sample solution.

For this purpose were prepared a series of standard solutions of hydro-alcoholic phenanthrene with concentration of the test substance 0.00005; 0.0001; 0.0002; 0.0003 and 0.0004 g/L. All measurements were performed on a spectrophotometer Agilent Cary Win. The absorbance of these solutions was measured in the wavelength range from 190 to 400 nm and a thickness of cuvette 1 mm. The results of absorbance dependency of standard solutions of phenanthrene represented from the wavelength are presented in figure 1.

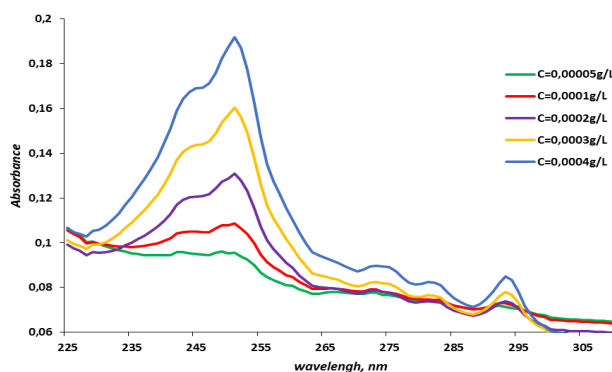


Fig. 1. The dependence of the absorbance of the standard solutions of phenanthrene from the wavelength

Then to the test solution with a known concentration of phenanthrene were added the different samples of humic acids with concentration of 0.01 g/L, and the absorbance was measured at the same wavelength.

Mathematical treatment of the obtained spectra, comprising the steps of smoothing and consideration of baseline were carried out with the program Assayer. Then determined the concentration of phenanthrene, absorbed by the molecules of the modified humic acids (Tab. 2).

Table 2

The results of calculation of the absorbed concentration of phenanthrene by humic acids

$C_{\text{init fen, g/L}}$	$C_{\text{abs, \%}}$		
	HA1	HA2	HA3
0,00005	42,85±10	66,66±11	86,66±13
0,0001	40,91±7	57,89±8	61,04±8
0,0002	27,50±6	30,00±7	39,24±5
0,0003	21,21±4	28,12±5	38,28±6
0,0004	17,99±4	20,69±3	26,70±5

Table 2 shows that the application of mechanochemical modification increases the humic acids binding ability towards phenanthrene. The use of thiourea as a modifying agent provides a phenanthrene absorption with the initial concentration of 0.00005 g/L with the HA3 up to 86.66% compared with HA1 (42.85%). With increasing of phenanthrene concentration the residua ratio of toxic substance in the solution increases, which points to the limited absorption capacity of humic acids. However, modification of humic acids leads to increase this indicator.

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